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THE KINETICS OF THE OXIDATION OF IODINE
BY DICHROMATE IONS IN ACID SOLUTION

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MASTER OF SCIENCE

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ABSTRACT

A study of the kinetics of the oxidation of iodine to iodate ion
by dichromate ions in acid aqueous solution was undertaken. Ionic
strength and temperature were maintained constant and the progress of
the reaction was followed by spectrophotometric analysis of unreacted
iodine extracted into carbon tetrachloride.

It was established that the reaction was $\frac{1}{2}$ order in I_2, but no
exact relationship was found with hydrogen ion or any hexavalent
chromium species. First order dependency on acid and H_2CrO_4 was
found to be a possibility, or at least a useful approximation, although
a more precise knowledge of all Cr(VI) equilibria relations at high
ionic strengths than is available would be needed for verification.
A multi-step rate determining mechanism is possible, although low
iodine solubility coupled with high required concentrations of other
constituents limit available techniques and would probably, in this
event, make determination of the complete rate expression difficult.

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1. Introduction.

Early work in the kinetics of the oxidation of iodide ions by acid dichromate solutions [1] resulted in orders of reaction that were not integral numbers or simple fractions. Brönsted's suggestion [2] concerning the addition of neutral salt to fix the activity coefficients of the ions resulted in more simple rate expressions [3] that were still only of an approximate order and were valid only over limited concentration ranges. It now appears that these investigators erred in assuming that the $Cr_2O_7^{-2}$ ion was the only hexavalent species present and that it must, perforce, be the oxidizing agent. More recent research [4, 5] presents equilibrium constants for several other Cr(VI) species present in acid dichromate solutions, and oxidation kinetic studies [6] suggest that $HCrO_4^-$ rather than $Cr_2O_7^{-2}$ is the agent.

A search of the available literature does not reveal any published investigations of the reaction

$$34H^+ + 3I_2 + 5 Cr_2O_7^{-2} \longrightarrow 10 Cr^{+3} + 6 IO_3^- + 17 H_2O$$
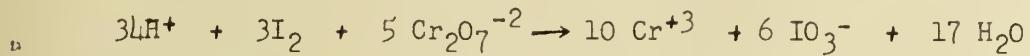
which proceeds, at the proper concentrations, at a rate well suited to such work. Additionally, a complete rate expression for this reaction would allow the proposal of possible mechanisms; a particularly interesting area of study since, neglecting an improbable three-electron transfer [7], either tetravalent or pentavalent chromium must be adduced as an intermediate.

2. Experimental Procedure.

The constituents used were reagent grade $HClO_4$, $Na_2Cr_2O_7$, and iodine. Ionic strength was maintained constant at 5.90 moles/liter ± 3% with reagent grade $NaClO_4$. The initial concentration of I_2 for each run was 4.15×10^{-4} M, the initial concentration of dichromate was varied from 0.918 M to 0.0184 M, and the perchlorate from 0.795 M to 0.0795 M. See Table 1. Temperature throughout was $25.00^{\circ}C$.

Since the concentrations used of acid and oxidizer required that the reaction be measured over periods ranging from three hours to six days, and since the initial concentration of iodine was of the same order of magnitude as the maximum solubility of I_2 in water, it was considered that further variations in reagent strength would serve no useful purpose. These concentrations allowed the progress of the reaction to be followed accurately only by measurement of iodine-containing species.

The possibility of buffering to a slightly acid condition followed by normal thiosulfate titration was eliminated by early measurements in which the reaction

$$8I^- + 6H^+ + IO_3^- = 3I_3^- + 3H_2O \quad (K = 5.8 \times 10^{55})$$
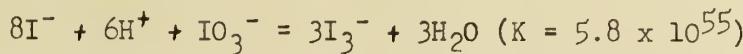
in conjunction with the rapid iodide-triiodide equilibrium increased the I_2 concentration so substantially as to obscure the reaction rate completely. It was also immediately determined that the reaction could not be followed directly with the available Beckman model DU spectrophotometer using the reacting solution; the dichromate absorbed light so heavily that it obliterated the iodine spectrum. Extraction of I_2 into carbon tetrachloride, however, proved rapid, and a thorough

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TABLE 1

CONSTITUENT CONCENTRATIONS

(moles/liter)

Run #	Total Cr(VI)	Gross Acid	$Cr_2O_7^{-2}$	$HCrO_4^-$	H_2CrO_4	H^+
1	1.836	0.795	0.692	0.125	0.328	0.467
2	1.836	0.636	0.722	0.129	0.262	0.374
3	1.836	0.477	0.751	0.131	0.202	0.275
4	1.836	0.398	0.768	0.133	0.168	0.230
5	1.836	0.239	0.799	0.1355	0.102	0.137
6	1.836	0.0795	0.832	0.138	0.034	0.0455
7	0.918	0.795	0.293	0.0820	0.250	0.545
8	0.368	0.795	0.0840	0.0439	0.156	0.639
9	0.184	0.795	0.0290	0.0258	0.100	0.695
10	0.0734	0.795	0.0061	0.0120	0.0490	0.745
11	0.0368	0.795	0.0017	0.0063	0.0272	0.768

shaking of equal volumes of CCl_4 and 1 M $Na_2Cr_2O_7$ followed by a few minutes' separation of phases produced no absorption in the CCl_4.

The extraction of I_2 was accomplished by pipetting 25 ml of the solution into 25 ml of CCl_4 in a glass-stoppered Erlenmeyer flask and shaking vigorously. The initial mixing extracted about 80% of the I_2 and essentially stopped the reaction; intermittent shaking for 20 minutes with 10 minutes' standing prior to reading concentration by means of the spectrophotometer gave reproducible results consistent with thiosulfate titrations of the iodine in the CCl_4 phase.

The distribution coefficient of iodine in the CCl_4-H_2O system was considered constant at 85.10 $\underline{/8/}$ introducing negligible error. With the two phases in contact during the run of highest concentrations (i.e., the most rapid reaction) there was no discernible change in the iodine concentration in the CCl_4 phase for 2.5 hours and a drop of six percent over a period of 20 hours.

The spectrophotometer was calibrated by plotting an absorption spectrum for I_2 in CCl_4 (see Table 2), ascertaining the validity of Beer's Law over the range of concentrations used, within the accuracy of the equipment available, and obtaining the slope of the Beer's Law plot by means of known solutions of I_2 in CCl_4. The slope of the Beer's Law plot was determined to be 1.12 millimoles per liter of I_2 per spectrophotometer absorbance unit (corresponding to a molar extinction coefficient of 893 $\frac{liters}{mole\text{-}cm}$) at a wavelength of 5150 angstroms, which was found to be desirable and was used. The same pair of matched silica cells was used throughout.

TABLE 2

SPECTROPHOTOMETER CALIBRATION DATA

λ	Absorbance (log Io/I)	
6250	0.157	
6000	0.025	
5800	0.313	0.00118 M I_2 in CCl_4
5600	0.488	
5400	0.808	Silica cells
5300	0.915	
5200	1.00	λ in Angstroms
5150	1.02	
5100	1.00	
5000	0.925	
4800	0.650	
4600	0.323	
4400	0.134	
4200	0.056	

At λ = 5150 Angstroms

$(I_2) \times 10^3$	Absorbance	ϵ (liters/mole-cm)
1.18 M	1.05	890
0.590	0.526	893
0.295	0.265	898
0.148	0.131	886

Initial attempts to use a separatory funnel to separate the phases for absorbance determination produced anomalous results; this was traced to a strong absorbance of stopcock grease (which was found to be readily soluble in CCl_4) at the wavelength used. Teflon stopcocks proved to be so recalcitrant in use that an alternative method was finally developed: a glass-stoppered Erlenmeyer flask was used to hold the two phases until extraction equilibrium was reached; a sample of the CCl_4/I_2 was then withdrawn with a pipette and discharged through a five-inch column of ceramic saddles which used the high wetting tendency of dichromate to remove any concomitant aqueous phase. This introduced no measurable error due to vaporization either of the I_2 or CCl_4.

It should be noted that, although solutions which did not contain $NaClO_4$ (i.e., solutions of the desired ionic strength without the salt added) always gave a time-concentration plot which extrapolated to the original concentration of iodine at zero time, those with $NaClO_4$ added often did not (see Figure 1). It was determined that salt used either directly or from a solution made from a freshly-opened bottle had no effect on the initial iodine concentration; however, after the bottle had been open (although capped) for several days, the contents immediately oxidized a small portion of the iodine. It was determined that the reaction was immediate (a very early reading was consistent with later readings) and that only the top layer of the $NaClO_4$ in the bottle was involved (if this was discarded, results extrapolated to the true initial concentration of iodine). No explanation for this is offered other than to point out the obvious formation of a more

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FIGURE 1

Sample Run Data Illustrating Impurities in $NaClO_4$

$(I_2)^{\frac{1}{2}}$ vs Time
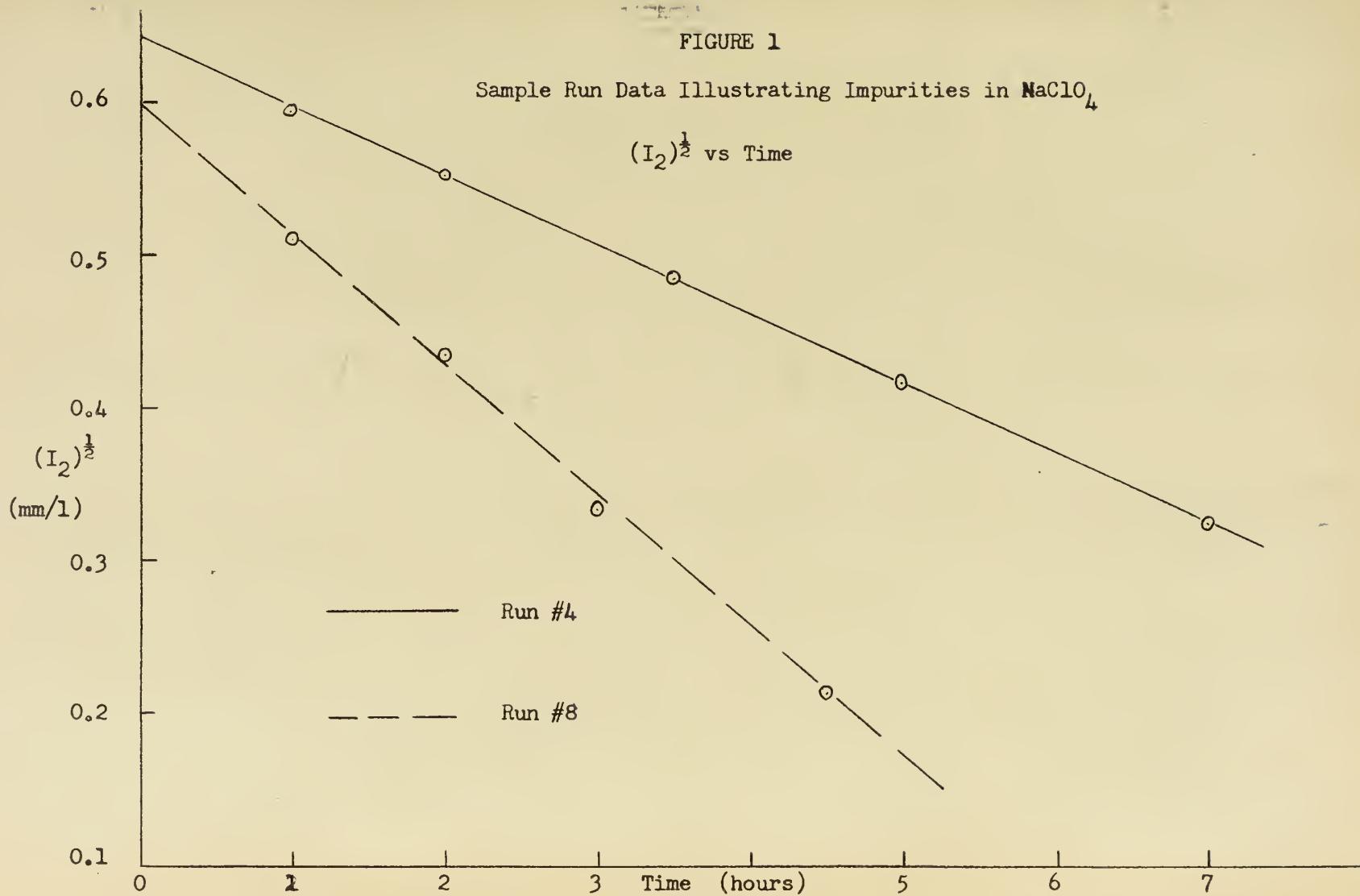
rapid oxidizing agent than perchlorate, in minute quantities, upon exposure to the atmosphere.

Solutions used were prepared as follows:

Iodine   A mass of solid iodine (Baker and Adamson, resublimed A.C.S. reagent grade, code 1800) sufficient to prepare 7 liters of approximately 0.8×10^{-3} M I_2 was dissolved in water and titrated against a commercially prepared thiosulfate solution (Hellige Inc. reagent concentrate R-1231C $\pm$ 0.1%) [9].

Perchloric Acid   Concentrated perchloric acid (J. T. Baker Chemical Co., "Baker Analyzed" reagent grade, 61.3%, A.C.S. specifications) was diluted to approximately 3 M and titrated against a commercially prepared sodium hydroxide solution (Hellige Inc. reagent concentrate R-1226C $\pm$ 0.1%) using a phenolphthalein indicator.

Dichromate   Sufficient sodium dichromate (Baker and Adamson, A.C.S. reagent grade, code 2204) was weighed out to yield approximately a 4 M solution, dissolved in water, and standardized against the thiosulfate solution prepared for the iodine [10].

Sodium perchlorate (G. F. Smith Chemical Co., reagent grade $NaClO_4 \cdot H_2O$) was used to maintain a constant ionic strength. This was accomplished by computing the ionic strength of the most concentrated solution used and adding sufficient salt to maintain this strength in the more dilute solutions. The assumption was made that $Cr_2O_7^{-2}$ was the only chromium-containing species; later computations showed that the maximum error introduced by this assumption was less than three percent.

Distilled water and carbon tetrachloride (Baker and Adamson, A.C.S. reagent grade, code 1554) were the media used in all instances.

3. Discussion.

The reaction proved to be unequivocally $\frac{1}{2}$ order in iodine (i.e., a linear relationship existed between time and the square root of the iodine concentration -- see Figure 2 and Table 3). This was determined early in the research and, due to the limitations imposed by reaction time and iodine solubility (see Table 1 and Experimental Procedure), the controlling constituent in every run was iodine; the minimum ratio of either acid or dichromate to iodine was over 40. In each set of readings a plot of time versus the square root of the iodine concentration, determined photometrically, yielded a straight line. There were no deviations throughout the range of concentrations used and most points were within a few percent of the best straight line.

The dependence of the reaction rate upon the acid and dichromate concentrations was less straightforward and was less satisfactorily determined. The concentrations of the various species were calculated by using the equilibrium relationships $\underline{/}4,5\underline{/}$ (formulas enclosed in parenthesis represent molar concentrations):

$$\frac{(H^+)(HCrO_4^-)}{(H_2CrO_4)} = 0.18$$

$$\frac{(HCrO_4^-)^2}{(Cr_2O_7^{-2})} = 0.023$$

A further relationship $\underline{/}5\underline{/}$,

$$\frac{(H^+)(CrO_4^{-2})}{(Cr_2O_7^{-2})^{\frac{1}{2}}} = 4.8 \times 10^{-8}$$

was not used in view of the small amount of CrO_4^{-2} formed, the difficulty to be encountered in handling the five interdependent unknowns involved,

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TABLE 3

EXPERIMENTAL RESULTS

Run #	Time (hrs)	Absorbance	I_2(millimoles/liter)	$k'(\frac{millimoles/liter}{hour})$
1	0.5	0.310	0.348	
	1.0	0.244	0.274	
	1.5	0.182	0.204	
	2.0	0.130	0.146	
	2.5	0.081	0.091	
	3.0	0.051	0.057	
				0.072
2	1	0.264	0.296	
	2	0.169	0.189	
	3	0.100	0.112	
				0.052
3	1.1	0.292	0.327	
	3	0.185	0.207	
	5.75	0.067	0.075	
				0.0318
4	1	0.316	0.354	
	2	0.272	0.304	
	3.5	0.208	0.233	
	5	0.155	0.174	
	7	0.093	0.104	
				0.0234
5	4	0.280	0.314	
	8	0.215	0.241	
	13.5	0.145	0.162	
	24.3	0.038	0.043	
				0.0088
6	33.25	0.299	0.335	
	82.75	0.230	0.258	
	109.50	0.204	0.228	
				0.00073
7	0	0.372	0.416	
	1	0.233	0.261	
	2	0.130	0.146	
	3	0.051	0.057	
				0.065

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TABLE 3 (Continued)

EXPERIMENTAL RESULTS

Run #	Time (Hrs)	Absorbance	I_2(millimoles/liter)	$k'(\dfrac{\text{millimoles/liter}}{\text{hour}})$
8	1	0.233	0.261	
	2	0.168	0.188	
	3	0.100	0.112	
	4.5	0.040	0.045	
				0.044
9	1	0.254	0.284	
	3	0.156	0.175	
	4.5	0.101	0.113	
	5	0.081	0.091	
				0.0297
10	1	0.270	0.302	
	3	0.204	0.228	
	5	0.151	0.169	
	6	0.124	0.133	
				0.0175
11	1	0.280	0.314	
	3	0.237	0.266	
	5	0.194	0.217	
	7	0.154	0.172	
	10	0.109	0.122	
				0.0115

and the results of previous work in allied fields [6] that did not indicate that CrO_4^{-2} might be the active oxidizing agent. For identical reasons such species as $HCr_2O_7^-$ were ignored.

In treating the data it was first assumed that (a) a hexavalent chromium species was the active oxidizer (no satisfactory alternative exists) and (b) only one rate-determining step was involved. The kinetic expression must then have the form

$$- \frac{d\,(I_2)}{d\,t} = k\,(I_2)^{\frac{1}{2}}\,(H^+)^x\,[Cr(VI)]^y$$

where Cr(VI) would probably be $Cr_2O_7^=$, $HCrO_4^-$, or H_2CrO_4. If this expression were valid, the slope of $(I_2)^{\frac{1}{2}}$ versus time for each run (defined as $-\frac{k'}{2}$) would yield the expression

$$k' = k\,(H^+)^x\,[Cr(VI)]^y$$

and a plot of $\frac{k'}{(H^+)^x}$ vs $[Cr(VI)]^y$ would, for the correct values of x and y, be a straight line. Only one solution was reasonably success-ful; with H_2CrO_4 as the Cr(VI) involved and both it and acid considered first order (x and y equal to one), Figure 2 resulted. This is con-sidered a distinct possibility, although some points fall in error by as much as 25 percent; it was assumed that all values of the equilib-rium quotients applied at the relatively high ionic strength used. This assumption is certainly not perfectly valid and might well be in sufficient error to account for the plotted discrepancies. If this is, indeed, the true solution, the rate expression is then given, roughly, by

$$-\frac{d(I_2)}{d\,t} = 8.9 \times 10^{-5}\,(I_2)^{\frac{1}{2}}\,(H^+)(H_2CrO_4)\ \text{mole}^{3/2}\ \text{liter}^{-3/2}\ \text{sec}^{-1}.$$

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FIGURE 2

$$\frac{k'}{(H^+)} \quad \text{vs} \quad (H_2CrO_4)$$

⊙ constant gross dichromate

△ constant gross acid
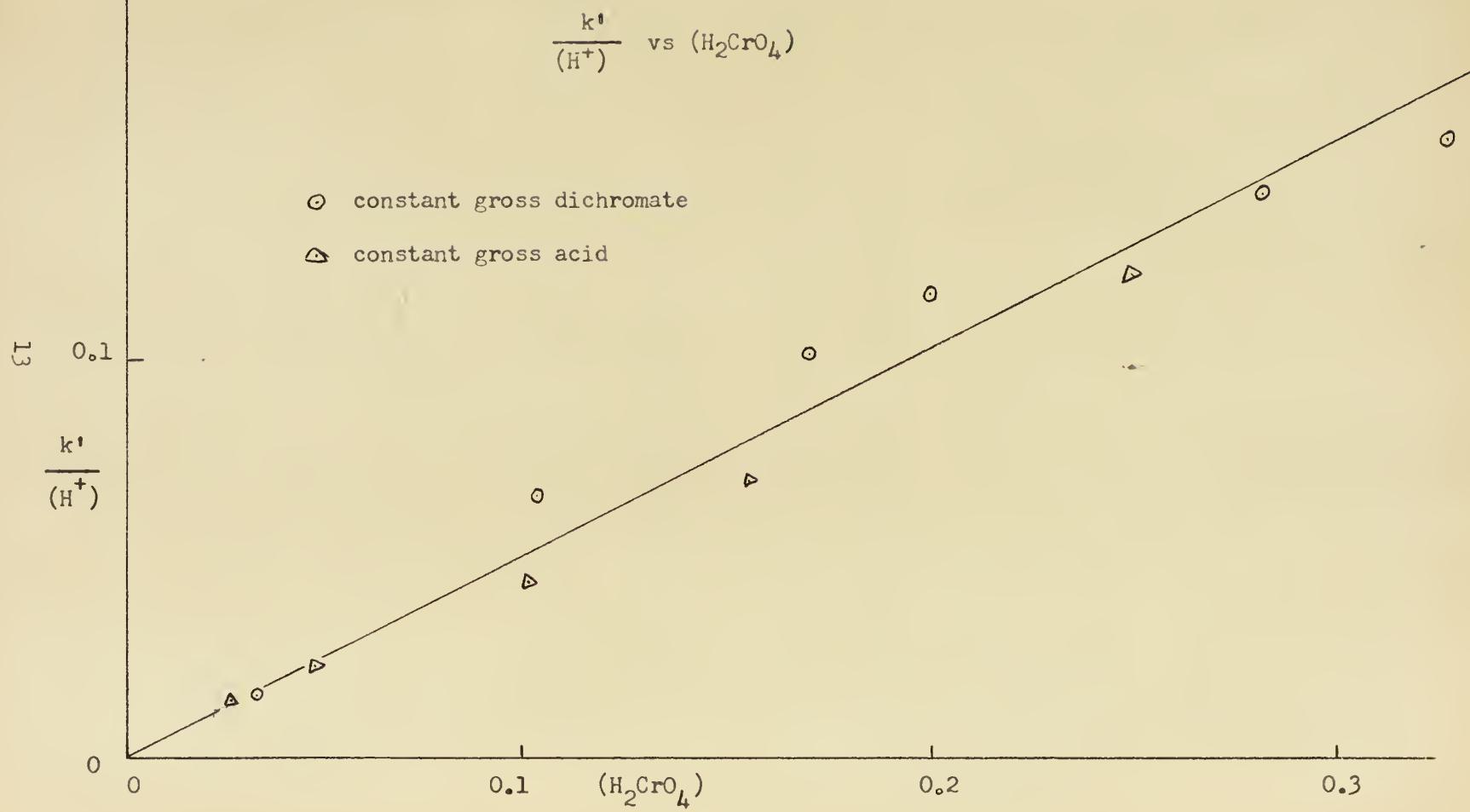
At the least it is a usable approximation within the limits of concentration and at the temperature used. Previous similar work does not, as published, consider H_2CrO_4 as the possible oxidizing agent [6], although concentrations used were much lower than in this work and possibly either H_2CrO_4 or $HCrO_4^-$ (the assumed agent) would be consonant with published data; in that event, present figures would indicate the former species is probably the oxidizer.

In searching for a more exact interpretation of the data, there was no satisfactory alternative to considering either an unknown side reaction as the complicating factor, or that there was more than one rate-determining step.

Similar procedures based on possible expressions of the form

$$ -\frac{d(I_2)}{dt} = k\,(I_2)^{\frac{1}{2}} \left[Cr(VI)\right]^{\,x} (H^+)^y \left[1 + a\,(H^+)^z\right] $$

or

$$ -\frac{d(I_2)}{dt} = k\,(I_2)^{\frac{1}{2}} (H^+)^x \left[Cr(VI)\right]^{\,y} \left[1 + a\,\{Cr(VI)\}^{\,z}\right] $$

also failed to give a satisfactory solution, although manual calculations limited the values of x, y, and z tried to those considered most probable.

No sources of error appeared to be large. Possibly the most important were the inherent accuracy of the spectrophotometer and the accuracy of pipetting carbon tetrachloride which has a lower viscosity than the aqueous solutions for which the pipettes were designed.

Since no incontrovertible expression for the rate of the reaction was arrived at, further work on this subject might prove interesting.

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However, it is considered that such investigations should initially be concerned with verifying or measuring appropriate equilibrium constants, and should then attempt to use a digital computer to (a) determine the concentrations of all species in the solution, and then (b) find the correct expression, possibly involving several rate determining steps. For instance, it is conceivable that one step utilizes $HCrO_4^-$ and another step H_2CrO_4; only exceptional experience or good fortune would allow such an expression to be discovered using ordinary trial and error methods. Continued investigations might also be concerned profitably with the use of somewhat higher temperatures to allow increased iodine concentration and reduced acid and dichromate. Final mechanism proposals might be greatly aided by use of induced oxidations, excellent examples of which are to be found in the literature [6].

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